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Vapor–solvent shift of the lowest frequency vibration of *p*-benzoquinone and toluquinone and the consequences for the vibrational and electronic spectral assignments

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Far-infrared (20–230 cm^{-1}) absorption spectra of *p*-benzoquinone-h_4,-d_4 and of toluquinone have been measured. In the vapor phase, the lowest frequency vibration of these three compounds is found at 88.9, 87.5, and 82.3 cm^{-1}, respectively. In the condensed phase the frequency increases by approximately 20 cm^{-1}. These measurements clarify assignments, based on this vibrational mode, of the visible absorption spectrum as well as of other vibrations. It is proposed that intermolecular forces are responsible for the large frequency shift and that the observed width in solution ($\simeq$24 cm^{-1}) is homogeneous, reflecting rapid relaxation processes of this large amplitude low frequency bending mode.

I. INTRODUCTION

p-Benzoquinone is a prototype molecule and it is therefore not surprising that considerable work has been done concerning the assignment of its electronic and vibrational spectra.[1-21] All experimental evidence is in agreement with D_{2h} symmetry for the free molecule. Of its 30 normal modes, 15 are Raman, 13 are infrared active, and two modes of a_u symmetry are inactive in both. The frequencies of these two modes have been obtained from an analysis of the vapor phase absorption spectra in the visible region.[1-3] The lowest frequency mode of the molecule is infrared active and corresponds to an out of plane distortion which takes the molecule into a boat form, its frequency of about 100 cm^{-1} is unusually low for a molecule of the size of *p*-benzoquinone.[8]

The lowest energy electronic states of *p*-benzoquinone are near degenerate, a fact that makes this molecule an interesting case to study the consequences of such an unusual electronic structure and has stimulated much interest but also makes the analysis of its spectra more complex. It has been shown that the excited electronic states can be fairly well understood in terms of local $n\pi^*$ excitations of the two C=O groups.[12,16,17] The bulb vapor phase absorption spectrum has been analyzed in detail by Hollas,[1-3] who relied for his assignment on the great analogy that exists with the low temperature single crystal spectrum; he showed that almost all of the observed bands of the singlet system can be understood in terms of only one of the two $n\pi^*$, namely the $^1B_{1g} \leftarrow {}^1A_g$ transition and used the "boat" vibration to locate the electric dipole forbidden origin. The frequency of this vibration increases by 35 cm^{-1} in the excited state and long sequences with this frequency interval are therefore observed in the vapor phase spectra taken at and above room temperature. More recently Ter Horst and Kommandeur[18] analyzed the jet cooled spectrum of *p*-benzoquinone and confirmed the main features of Hollas assignment but located the origin as magnetic dipole transition at about 15 cm^{-1} to higher energy. The intensity of the magnetic dipole origin is comparable to the intensity of vibronic bands belonging to the symmetry allowed $^3A_u \leftarrow {}^1A_g$ singlet–triplet system whose origin lies about 1500 cm^{-1} to lower energies. Even though the observed band contours favored the magnetic dipole assignment this new value for the energy of the origin raises problems as it requires the frequency of the boat vibration to be some 20 cm^{-1} lower at about 87 cm^{-1} than in previous assignments, which relied on infrared spectra. The I.R. absorption spectra of *p*-benzoquinone as crystalline powder or in solution of CCl_4[10] or benzene[4] show this band at 108 cm^{-1} and its frequency does not seem to vary between different solvents or in going to the crystal phase. The new assignment of this mode therefore requires a 25% increase in frequency (or in other terms a 50% increase in the force constant) in going from vapor to condensed phase. This is quite unusual especially since none of the higher frequency modes for which measurements have been made in vapor phase and, in solution, show any significant frequency shift. As the boat vibration plays a key role in the assignment of the vapor phase spectra and in order to ascertain such an unusual frequency shift it

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seemed desirable to make a direct measure of its frequency in the vapor phase. In this paper we report the infrared absorption spectra in the range of 20–230 cm^{-1} of fully protonated and deuterated *p*-benzoquinone and of toluquinone, the methyl substituted derivative, in vapor phase and in solution and discuss the consequences of these measurements for the assignment of the visible absorption spectra. The large vapor to condensed phase shift is confirmed and possible contributions to this change in frequency are discussed.

II. EXPERIMENTAL

Commercial *p*-benzoquinone and toluquinone (Eastman Kodak) were purified by sublimation *in vacuo*. *p*-Benzoquinone-d_4 was synthesized from perdeutero benzene (isotopic purity > 99.8%). A glass cell (length 13 cm) with 2 mm polyethylene windows was used for the vapor phase spectra. The vapor pressure was controlled by maintaining the cell at a constant temperature of about 100 °C. Some solid *p*-benzoquinone or liquid toluquinone deposited at the cell windows. The reference spectrum for the vapor phase was run with the filled gas cell at ambient temperature permitting to take into account these depositions. The remaining feature at about 70 cm^{-1} is due to the frequency shift with temperature of the polyethylene band in this region.

Solution spectra were taken in a 1.5 mm cell with high density polyethylene windows of 1 mm thickness and were ratioed with the CCl_4 solvent absorption.

All far infrared spectra were recorded by a POLYTEC FIR 30 interferometer working under vacuum equipped with a Cathodeon Golay detector and a high pressure Hg source. The typical spectral range of 20–230 cm^{-1} was defined by 12 μm Mylar beam splitter, appropriate optical filters (short wavelength cutoff at 40 μm) and a sampling interval of 10 μm. Acquisition, FFT and data handling was carried out on a Hewlett-Packard 9835 A calculator. The spectra were calculated with a spectral element of $\Delta\nu = 0.25$ cm^{-1}; the effective resolution, defined by the apodisation function, was $\Delta\nu_{eff} = 1.4$ cm^{-1} for the vapor phase spectra and twice this value for the solution spectra.

III. RESULTS

Figure 1 shows vapor phase spectra between 50 and 125 cm^{-1} of *p*-benzoquinone ($-h_4$ and $-d_4$) at 380 K and Fig. 2 the vapor and condensed phase (liquid and CCl_4 solution) spectra between 30 and 180 cm^{-1} of toluquinone. No other infrared absorption bands were observed in the spectral range of 20 to 230 cm^{-1}.

The sharp absorption band of the vapor phase spectra represents the *Q* branch of the boat vibration ν_{26} of *p*-benzoquinone using the numbering of vibrations of Ref. 8; the observed width of this band is limited by the resolution of the spectra, the intrinsic width can safely be estimated to be less than 1 cm^{-1}. The differences of the experimentally observed widths are not significant but reflect in part slight instabilities during the experiment (e.g., deposition of material on the cell windows).

The rotational contour calculations were done for *p*-benzoquinone-h_4 using the program ASYROT provided by Ramsay; the same rotational constants as given by Hollas for the molecule in the electronic ground state were used and only a type *C* contour calculation was performed as the out of plane transition moment for ν_{26} is well established. The calculated width of the *Q* branch (<0.1 cm^{-1}) is remarkably small and the overall contour agrees well with the experimental spectra, fully confirming all previous symmetry assignments of this band.

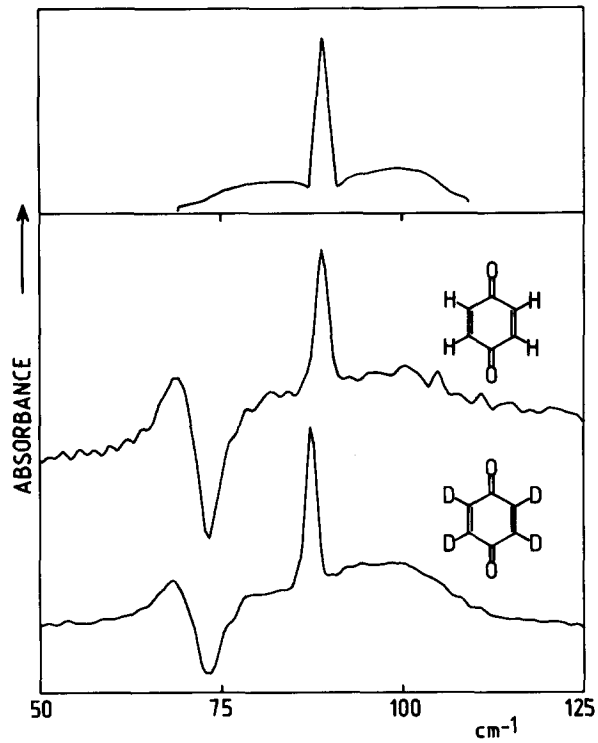

FIG. 1. Vapor phase spectra of *p*-benzoquinone. Top: calculated spectrum; Bottom: experimental spectra. The temperature for all spectra is 380 K. The width of the central *Q* branch of the calculated spectrum is less than 0.1 cm^{-1}, for a better comparison with the experiment it has been given a triangular shape with the same integrated intensity and the width of the experimental spectra. The dispersion shaped feature at $\simeq$70 cm^{-1} is due to the polyethylene window and reflects the red shift, as a function of temperature, of a weak absorption band of this material at this frequency.

As solution spectra of *p*-benzoquinone have been reported previously[4,10] only the spectrum of toluquinone in CCl_4 was recorded.

The spectrum of liquid toluquinone was obtained as a "by product" of the vapor spectrum. The line shape of both condensed phase spectra can be fitted well within experimental accuracy with a Lorentzian.

All experimental observations together with some relevant literature data are summarized in Table I.

IV. DISCUSSION

A. Description of the vibration

The three vibrations of b_{3u} symmetry in *p*-benzoquinone involve displacements of the hydrogen atoms and the carbon and oxygen atoms of the carbonyl group perpendicular to the plane defined by the remaining carbon atoms. For the lowest frequency vibration ν_{26},

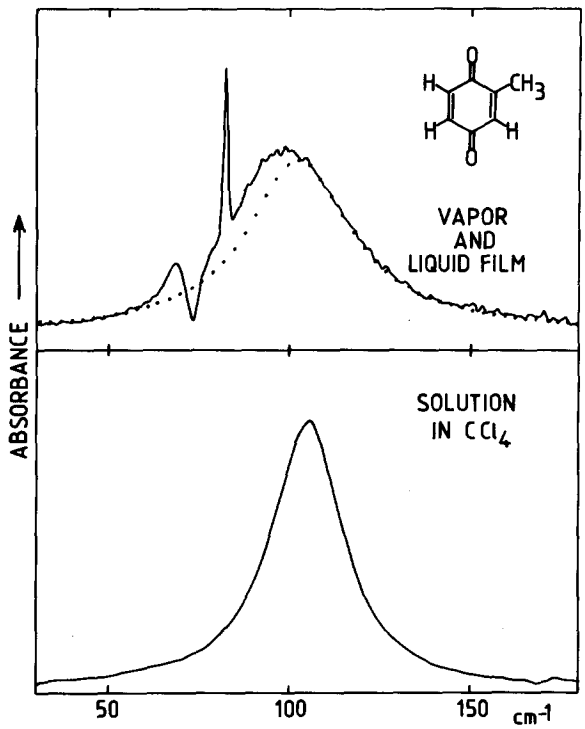

FIG. 2. Vapor and condensed phase spectra of toluquinone. Top: spectrum at 380 K of the vapor cell; as toluquinone deposits as liquid film on the cell windows, both the vapor phase and this liquid film contribute to the spectrum. The sharp feature at 83 cm^{-1} represents the Q branch of the vapor spectrum, after subtracting the P and R branches the liquid spectrum is obtained as a large band centered at 103 cm^{-1} and having a Lorentzian line shape with a FWHM of 35 cm^{-1} (dotted line). For the feature at 70 cm^{-1} see caption of Fig. 1. Bottom: solution spectrum in CCl_4 at 295 K.

these displacements are in phase—the motion of the hydrogen atoms can be neglected and the contributions of the ring bending and C=O bending are approximately equal.[9] This description of the vibration accounts for the small H_4/D_4 isotope effect and leads also to a correct value of the infrared absorption intensity of this band. The rms value of the angle between the C=O group and the plane formed by the central four carbon atoms is found to be $3.3° \cdot (2n + 1)^{1/2}$, where n is the vibrational quantum number.

In spite of this large amplitude (15 ° for the tenth vibrational level), the vibration is very harmonic. This was already suggested by Hollas[2] based upon the constancy up to eight quanta of the +35 cm^{-1} sequence interval in the visible absorption spectrum. Our measurements confirm this behavior and give a quantitative limit. Defining as customary the energy levels of the harmonic oscillator by $E_n = (n + 1/2)\hbar\omega_0[1 - (n + 1/2)\delta]$, we find that δ is not larger than 5×10^{-4}.

B. Spectral reassignments

The direct measurement of the ground state frequency of ν_{26} in the vapor phase clarifies a number of questions raised in previous work on the vapor phase spectra of p-benzoquinone in the visible region. It leads to corrected values for the excited state frequencies of all vibrations appearing as vibronic origins in this spectrum and leads in particular to new values in the ground state for the two infrared and Raman inactive vibrations of a_u symmetry. We shall not discuss here the detailed assignment of the visible vapor phase spectra of p-benzoquinone which, in our opinion, still contains a number of questions to be resolved by a comparative study with the spectrum of toluquinone presently underway.[221] Our measurements confirm the assignment of Ter Horst and Kommandeur[18] concerning the vibronic origins of the $^1B_{1g} \leftarrow A_g$ transition, there are small discrepancies ($\lesssim 3$ cm^{-1}) between the frequencies reported by these authors and the values for the band centers that can be derived from Hollas[1] data. Determinations of frequency differences involved in sequence bands as well as of the sum of vibrational frequencies in the ground and excited state as measured by the energy difference of the corresponding hot and cold bands are certainly precise and agree to ~ 1 cm^{-1} for different authors. Combined with the present measurements of the ground state frequency of ν_{26} these yield the following data: The origin of the $n\pi^*$ $^1B_{1g} \leftarrow {}^1A_g$ transition is located at 20 047 cm^{-1} for both p-benzoquinone-h_4 and -d_4, and the frequencies of vibrations involved in the most prominent false origins of this transition are as summarized in Table II. For the d_4 compound, the frequency differences between ground and excited states are now quite close for the vibrations ν_{26} and ν_{23}; this might account for the failure by Hollas to observe both sequence intervals separately. The assignments of the two vibrations of a_u symmetry yield an excellent agreement with the predictions of the Teller–Redlich product rule

TABLE I. Frequencies (ν) and linewidths ($\Delta\nu$ = FWHM) in cm^{-1} of the lowest frequency mode observed in the infrared spectra of p-benzoquinone and toluquinone in vapor and condensed phase.

	Vapor phase		CCl solution 295 K		Benzene solution[b] 295 K	
	380 K,	Q branch				
Compound	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	ϵ_{max} (ℓ mol^{-1} cm^{-1})
p-benzoquinone -h_4	88.92	2.04	108	24[a]	108.5	25 ± 10%
-d_4	87.48	1.78			106.5	25 ± 10%
					Liquid at 380 K	
					ν	$\Delta\nu$
Toluquinone	82.30	1.36	104.8	23.4	103	35

for both electronics states. The ground state values of the three vibrations cited in Table II differ by about 20 cm^{-1} from those given Becker, Charney, and Anno[8] and used for the adjustment of force constants in normal mode calculations.[9] For the two low frequency vibrations ν_{26} and ν_{23}, the relative change is quite large and some of the out of plane bending force constants should therefore be revised accordingly.

C. The solvent shift

The large vapor to condensed phase shift of the boat vibration ν_{26} clearly was quite unexpected and therefore is an understandable cause for the misassignments discussed in the preceeding section. In general, the solvent shifts of internal vibrations of molecules are thought to be small, exceptions are of course observed and have been studied for molecules forming associations among themselves or with solvent molecules. Sizable *red* shifts are observed for very strong infrared bands and are rationalized by dielectric effects. The very strong asymmetric C=O stretching vibration of *p*-benzoquinone is such an example. Its frequency decreases from 1682 cm^{-1} in the vapor phase to 1668 cm^{-1} in a solution of CCl_4. All other fundamentals, reported previously, changed by a few wave numbers only. ν_{26} is a fairly intense infrared band and undergoes a large *blue* shift in the condensed phase. Measurements on toluquinone confirm this behavior; in addition the width of the absorption band in solution is quite large for both molecules.

In order to ascertain whether the behavior of these two molecules is exceptional we have made a literature search on the low frequency bending modes in vapor and condensed phase of *p*-disubstituted benzenes. Even though the data are incomplete (the most extensive study of this class of compounds is found in a series of papers by Green and Harrison,[23] it seems that the boat vibration of these compounds follows a similar behavior. The vapor phase/solution frequencies for *p*-difluoro-benzene are given as 156/165 cm^{-1} and for *p*-xylene as 132/152 cm^{-1} for example.[24] The lowest frequency vibrations of other substituted benzenes exhibit similar shifts. For the lowest frequency bending mode of naphthalene an analogous behavior is observed. Its frequency of 166 cm^{-1} in the vapor phase[25] increases to 181–184 cm^{-1} in condensed phases.[26] This phenomenon therefore seems to be more general and apparently has gone quite unnoticed, in part certainly due to the sparseness of far infrared data especially in the vapor phase. The frequency of the other vibrations (except for the cases mentioned above) remains approximately the same in going to the condensed phase. The environment does not alter significantly the electronic structure and therefore does not change the intramolecular force constants. The increase in frequency of the boat vibration, or more generally of all large amplitude low frequency modes, must be due to repulsive intermolecular forces. These vibrations "feel" most strongly the cage of the condensed phase environment. As the repulsive part of intermolecular potentials is quite steep and as the amplitude of the motion is large, it is understandable that the precise nature of the environment is less important. The vapor to condensed phase shift is large while the solvent dependence is smaller.

For *p*-benzoquinone and toluquinone the frequency shift amounts to about 20 cm^{-1} which is 25% of the vapor phase frequency; the absorption band in solution has a FWHM of ~24 cm^{-1} and has a purely Lorentzian line shape. This suggests that the band is homogeneously broadened. The strong coupling with the environment, as evidenced by the frequency shift, makes both population and phase relaxation very efficient. Population relaxation of very low frequency modes is enhanced by virtue of the smaller energy difference with the bath modes, while for higher frequency vibrations it's often thought to make a minor contribution only to the total linewidth.

Our results suggest that far-infrared studies of vibrational modes such as discussed here provide a useful experimental approach to the understanding of relaxation processes in liquids.[27]

TABLE II. Vibrational frequencies (cm^{-1}) of *p*-benzoquinone-h_4/d_4 in the vapor phase.

	Ground state ^1A_g	Excited state $n\pi^*$ $^1B_{1g}$
$\nu_{26}b_{3u}$	88.9/87.5	124/122
$\nu_{23}a_u$	330/297	379/335
$\nu_{22}a_u$	989/788	926/744

V. CONCLUSION

It seems that whatever unexpected property a molecule is capable to exhibit, it will be found in *p*-benzoquinone. From the observation of an apparent dipole moment in this centrosymmetric compound[28] to the near degeneracy of its lowest electronics states. More seriously, this study showed that the "unexpectedness" of the frequency shift of the boat vibration, which has led to spectral misassignments, reflects a lack of far-infrared data rather than an exceptional behavior of the molecule. On the other side this sensitivity to condensed phase environment might make such low frequency bending modes useful probes of the liquid and solid environment. In *p*-benzoquinone the excited state ($n\pi^*$ $^1B_{1g}$) frequency of ν_{26} increases from 124 cm^{-1} in the gas phase to 137 cm^{-1} in a neon host[20] and to 147 cm^{-1} in the pure crystal.[11] At this point clearly more experimental and theoretical work is needed in order to explore these ideas.

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